STRUCTURAL TRANSFORMATIONS OF ICE AT HIGH PRESSURES VIA MOLECULAR DYNAMICS SIMULATIONS(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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A simple classical model for ice is used to molecular dynamics (MD) simulation, which studies the structural transformations under high pressures, such as ice VIII to VII and X. In this model pair potentials between pair of atoms are assumed of a simple form originally developed by Kawamura et al. and also a three-body potential representing the H-O-H angle dependence is assumed. Starting with a stable ice VIII at low pressure and low temperature, we have carried out two different runs, one with increasing pressure keeping the temperature constant (we call simulation I) and the other with increasing temperature under constant pressure (we call simulation II). In these MD simulations we have obtained the structural transformations from ice VIII to VII, followed by the transformation to X for the simulation I. These results are compatible with recent experiments on high pressure ices.

Ice is one of the most popular materials and is known that it has various (at least 10) different stable crystalline structures. They are still unknown in high pressures[1]. In this study we focus on the ice X and the related structures, VIII and VII, as well and the structural transformations between them. In ice X, the most specific is seen in that hydrogen atoms in this structure can be located on the mid point of the near-neighbor two oxygens, so that there is no picture of water molecules. Ice X is obtained only at very high pressures, the transition to this phase is accurately yet unknown because of difficulties of experiments under high pressure.

Under such circumstances the main purpose of the present work is to investigate the structural phase changes of ice at high pressures via a molecular dynamics simulation using recently developed pair and three-body effective potentials between atoms. This model differs from any rigid molecular models which are often used as models of water or ice, but are useless for the present work, high-pressure ice in which water molecules should significantly be changed in structures from those of normal water molecule. In the present model the system is simply composed of two different atoms, H and O, without any computational condition of forming water molecules; the pair interaction and the three-body interaction recently proposed for water and low-pressure ices by Kawamura et al.[2] were used. Before carrying out the MD simulation it has first been confirmed that such model potentials give a reasonable result for ice VIII in comparison with other rigid molecular models. In MD simulation we have used the algorithm of flexible cell originally developed by Parrinello and Rahman.

Figure 1 shows the partial pair distribution functions g_{OH}, (a) for ice VIII through X, obtained by the simulation I (constant temperature MD) and (b) for ice VIII through VII, obtained by simulation II (constant pressure MD). Figure 1(a) shows dramatic changes of structures upon applying pressure, indicating clearly that the final structure obtained by the present simulation I yields two hydrogen atoms of each water molecule and hydrogen-bonded H atoms in the net work of water molecules being equivalent. In other words, the hydrogen bonds are located at the mid point of two near-neighbor oxygen atoms. This is a structural characteristics of ice X. Between ice VIII and X appears ice VII. Ice VII is a disordered structure with respect to

hydrogens, whereas the ice VIII is an order structure with a non-vanishing value of a well-defined order parameter (projection of the dipole to c direction) in respective sublattices. On the other hand, figure 1(b) shows no drastic change of structures with only quantitative changes. implying no such a change of hydrogen bonds as in high-pressure ice X just mentioned above.

Conclusion and discussion of the present simulation: we have shown the following results of interest: (1)Ice X was obtained from ice VIII, and the hydrogen bonds are substantially different for both structures. (2)During the structural transformation from ice VIII to ice X on applying pressure, another stable phase of ice VII appears. (3)The structure of ice VII thus obtained differs from that of ice VII obtained by heating of VIII at a normal pressure. The latter is accompanied by the defects induced by rotation of water molecules(orientational defects), while the former contains the defects by exchange of two stable sites of a hydrogen-bond atom between two near-neighbor oxygen atoms(ionic defects). (4)The values of pressures obtained by the simulation is remarkably higher than the corresponding experimental values[3]. This is nothing but to show that the present model is not sufficiently good to the pressure computation. Since the pressure is proportional to the derivative of the total energy with respect to the volume of the system, it should be rather sensitive to tails of weak potentials, which are very difficult to know in general. (5)The model potentials which we have used in the present work are also possible to apply to other structural transformations of ice. This will be discussed elsewhere.

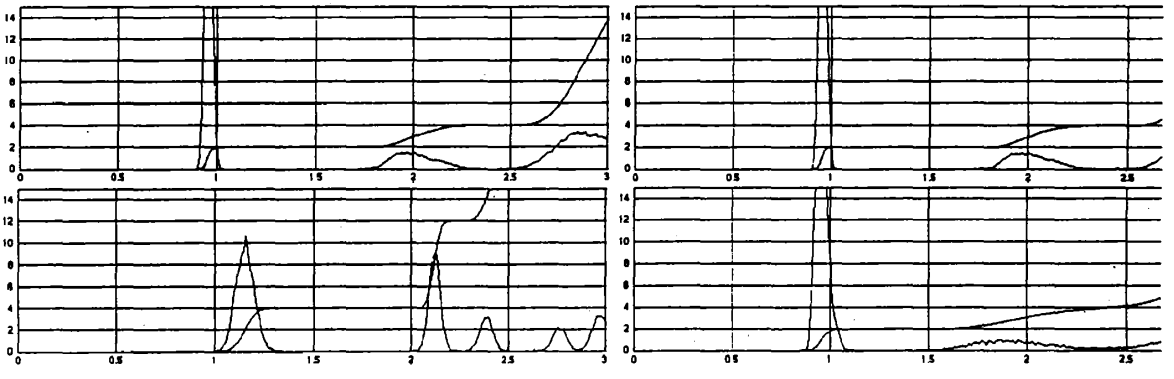

Figure 1: The partial pair distribution functions g_{OH} (a: left) for ice VIII (upper) and X (lower), obtained by the simulation I and (b: right) for ice VIII (upper) and VII (lower), obtained by simulation II.

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